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(54) ENZYMATICALLY DISPERSIBLE NON-WOVEN WEBS AND PADS



(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 3M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Non-woven fabrics have gained wide acceptance for use in disposable products because of their relatively low cost of manufacture as compared to that of more conventional fabrics made by weaving or knitting processes. They have a wide variety of uses including surgical dressings, incontinence pads, diapers, cigarette filters, quilting or padding, cleaning materials and the like. Such non-woven fabrics are commonly available commercially in a wide range of fabric weights from as little as about ten grams per square meter to as much as about 200 or more grams per square meter.

These items require greater or less dry- and wet-strength according to the use for which they are designed. Extremely low strength materials such as those used for facial cleansing tissues often are required to have substantially no wet-strength. Other items such as bandages should have relatively high dry- and wet-strength to permit use over a period of time in the presence of body fluids or water.

Many attempts have been made to provide disposable sanitary items such as diapers, and a certain measure of commercial success has been attained. Thus, for example, U.S. patents 3,636,952; 3,480,016; 3,070,095;

3,214,323; 3,406,688, describe so-called disposable sanitary products.

Various non-woven fabrics have been designed for use in sanitary absorbent products such as diapers and the like which are designed to disintegrate or disperse when the product is placed in water, as in the household toilet. In an effort to provide non-woven fabrics which retain their integrity in the presence of more than limited quantities of aqueous fluids, yet allowing for dispersal of the fibers of the web when this is placed in water, a number of bonding methods have been proposed. Intermittent or random patterns of adhesive or binder resin to bind fibers is disclosed in U.S. patents 2,039,312 and 3,616,797, and other patents; use of stitching is disclosed in U.S. 2,010,433; use of water-soluble binders in U.S. 2,999,038; 3,310,454; 3,370,590; 3,546,716 and 3,554,788 and possibly others; and the use of water-soluble fibers as such is disclosed in e.g. U.S. 3,347,236 and 3,550,592. In U.S. 3,480,016 there is described an absorbent product which is water-dispersible when an acid or alkali is added to the water, in which a random web of non-woven fibers is bound by means of an acid or alkali sensitive binder.

The water-dispersible products of the prior art, as disclosed in the above-mentioned patents, are not entirely satisfactory for the purposes designed. Some of them are inherently disintegratable in the presence of water, thus maintaining their integrity only in the presence of limited quantities of aqueous fluids. The non-woven products of U.S. 3,480,016, although seemingly stable in water alone, are apparently to a degree unstable in acidic or basic aqueous systems

which have a pH in the range of that of physiological (body) fluids. In any case it appears that it requires use of added acid or base to disposal systems for effective disposal of these webs.

While the use of acid- or base-sensitive binders for non-woven webs, which permits disposal after disintegration by means of an acidic or basic reagent, appears to present the best solution thus far advanced for the problem of disposable absorbent materials, this approach is still not believed to be practical. The repeated use of acids or alkalis, whether dilute or concentrated, is believed to be detrimental in the long run to sewage disposal systems depending upon natural organisms for degradation and disposal of sewage. Further, if large numbers of people were to employ such materials in conjunction with municipal disposal systems involving a large central treating station, it is believed that problems would arise in connection with accumulation of acidic or basic materials at some point in the system. Moreover, the handling of strong acids or bases entails hazards to the persons who come in contact with such materials, particularly children, and of course the association of such materials with the use of diapers for small children must be a distinct disadvantage.

This invention contemplates provision of diapers and other sanitary products which are inexpensive and disposable after a single use, which possess good wet-strength so as to provide structural integrity during condition of use without the need for reinforcement by woven fabrics, yet which are readily and safely disposed of in domestic disposal systems with the aid of materials which cause no harm to or interference with the efficiency of such sewage disposal systems.

The present invention provides a self-supporting, non-woven composite web which is dispersible in an aqueous medium containing an enzyme, consisting essentially of a non-woven web of fibres and in combination therewith a water-insoluble, normally solid, enzyme-disintegratable binder which consists of a polymer of at least one ethylenically unsaturated monomer covalently bonded with a naturally-occurring, enzyme-degradable, water-soluble polymeric material, the binder being present in an effective amount ranging from 0.3 percent to 100 percent by weight of the fibres in the non-woven web, sufficient to impart to the non-woven web a wet-strength in an aqueous medium in the absence of an enzyme of at least 0.5 kg/cm² and to increase the resistance to dispersion of the web in plain water whilst permitting dispersion of the non-woven web in a period ranging from 5 to 30 minutes in an aqueous medium containing

an enzyme capable of disintegrating said binder.

Preferably, the composite webs of the invention are resistant to dispersion in water free from enzyme for periods greater than 30 minutes. The dry-strength of these materials is generally greater than their wet-strength, and is preselected so as to be commensurate with the use for which they are designed. The wet-strength, however, is at least 0.5, e.g. from 0.5 to 10 kg per cm², and is preferably preselected to fall within the range of 0.7 to 10 kg per square cm, as that range encompasses substantially all of the uses to which the articles of the invention are likely to be put.

Non-woven webs useful in the practice of the invention may be prepared by carding, garnetting, air deposition, water deposition or any of the various techniques known in the art for the purpose. The fibres may be oriented predominantly in one direction as in a card web or card web laminate, if desired. Alternatively, they may be substantially isotropic, that is they may have equivalent strength in all directions. Useful fibres for the purposes are those of viscose rayon, cotton, wool, silk, cellulose, linen, hemp, wood fibres and the like, or purely synthetic fibres, e.g. regenerated cellulose, nylon, or polyester.

Preferred fibers for the purpose of the invention are natural fibers which are ultimately biodegradable. The length of fiber that can be employed is not critical, but it is preferred to use relatively short fibers, e.g. those having lengths between three to 12 millimeters. The non-woven webs thus produced can have a weight of the order of ten to 100 or more grams per square meter depending upon the end use. For example, a weight of from 20 to 60 grams per square meter is preferred for use as a diaper liner.

A convenient method for producing the non-woven webs is by any of various techniques known to the art, such as carding, garnetting, air deposition, and water deposition, e.g., by the Fourdrinier process as in paper making. If desired, the web can be calendered to a smooth, hard finish.

The binder employed in the invention is a water-insoluble polymer of at least one ethylenically unsaturated monomer, covalently bonded with a naturally-occurring, enzyme-degradable, water-soluble polymeric material. Exemplary of such are the reaction products with gelatin disclosed in U.S. patent 3,507,661. The polymers reacted with gelatin in these binders have a molecular weight of at least 10,000 and a degree of polymerization of at least 50, and preferably are of a molecular weight such that they have a glass transition temperature (T_g) which is substantially independent of the molecular weight of the polymer.

The water insoluble polymer may be a vinyl polymer. The polymers employed are required to have substituent groups, either pendant or terminal, which are reactive with the water-soluble, naturally-occurring polymers. Such vinyl polymers are polymers and copolymers of addition-polymerizable vinyl monomers which have substituent groups reactive with compounds having active hydrogen.

The term "active hydrogen" used herein is well known and commonly used in the art, and means active hydrogen as measured and determined by the method described by Zerewitinoff, J. Am. Chem. Soc. 49, 3181 (1927).

Illustrative of the polymers and copolymers of addition-polymerizable vinyl monomers useful in the practice of the invention are those polymers having repeating vinyl or vinylidene units, at least one mol percent and preferably from five to 30 mol percent of which contain one or more groups reactive with active hydrogen atoms. Although the molecular weight of these polymers can vary over a wide range, they generally speaking have a molecular weight ranging from 1,000 to several million or more.

A preferred class of copolymers are those that have a molecular weight such that the glass transition temperature (T_g) is substantially independent of the molecular weight, as described in J. Poly. Sci. 3A, 3579 (1965).

These vinyl polymers can be homopolymers or copolymers in which vinyl monomers having reactive substituent groups are copolymerized with vinyl monomers which do not have reactive substituent groups. Exemplary of monomers providing reactive substituent groups for the purpose are those including epoxy-containing monomers, e.g. glycidyl acrylate, glycidyl methacrylate and 3, 4-epoxybutens-1; N-methylol amide monomers, e.g. N-methylol acrylamide, N-methylol methacrylamide; aldehyde-containing monomers, e.g. acrolein, methacrolein or acetals or bisulfite addition products thereof and methyl vinyl ketone; alpha-haloesters, e.g. vinyl alpha-chloroacetate and aziridine-containing monomers, e.g. N-allyl aziridine and acryloxyalkylaziridine; and anhydrides, e.g. maleic anhydride. Vinyl monomers that may be employed in the preparation of copolymers with monomers containing a reactive substituent group include acrylate esters, e.g. methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate and 2-ethylhexyl acrylate; vinyl esters, e.g. vinyl acetate, vinyl propionate; olefins, e.g. ethylene, propylene, styrene, vinyl cyclohexene; dienes, e.g. 1, 3-butadiene, isoprene, chloroprene; vinyl ethers, e.g. methyl vinyl ether, butyl vinyl ether and octadecyl vinyl ether; amides,

e.g. acrylamide, methacrylamide, vinyl pyrrolidone; and acrylonitrile. Since the preparation of polymers and copolymers of the above monomers is extensively described in the literature, further elaboration is not necessary for a complete understanding of this invention. U.S. patent 3,242,123, for example, provides an illustration of the preparation of co-polymers useful in the practice of this invention. The reactive polymers generally are prepared in solution in an organic solvent or in emulsion and are utilized as such in the preparation of the enzyme degradable binders used in the practice of this invention.

The naturally-occurring, water-soluble, enzyme-degradable polymers which are reacted with (covalently bonded with) the above vinyl polymers to form the enzyme-disintegratable binder for use with the non-woven web contain active hydrogen groups in their structure, which can react covalently with the vinyl polymers because they have one or more imide, amide, amino, hydroxyl or carboxyl groups in their structure. They may be soluble in water to form a true solution, but in some cases form a sol or colloidal solution. The use of the term "water soluble" herein in connection with these naturally-occurring polymers is intended to refer to both true solutions and colloidal solutions. They are commonly capable of forming self-supporting films by evaporation of water solutions of the polymer.

Exemplary of such naturally-occurring polymers which are useful in the preparation of the binder used in the non-woven web composite of the invention include both animal and vegetable proteins such as, for example, albumins, e.g. serum albumin, egg albumin, ricin, leucosin and legumelin; globulins, e.g. serum globulin, myosin and myogen from muscle, edestin from hemp, and grain globulins; prolamines, e.g. zein, harden from barley, and gliadin from wheat; glutelins, e.g. glutenin from wheat and maize, and oryzein from rice; protamines, e.g. salmin and culpein; scleroproteins, e.g. collagen, gelatin, animal glue, elastin and fibroin; phosphoproteins, e.g. casein and vitellin; and glyco-proteins, e.g. mucins, mucoids and ovalbumin.

Examples of film-forming polysaccharides that may be used as the enzyme-degradable polymer component of the enzyme-disintegratable binder for the fibers in the non-woven fabric of the invention include starch, glycogen, inulin, amylose, amylopectin; the seaweed polysaccharides, e.g. algin, propylene alginate and other algin derivatives, carrageenan, fucoidan, laminaran and agar; the exudate gums, e.g. gum arabic, gum ghatti, gum karaya, tamarind gum and

tragacanth gum; and other gums, e.g. locus bean gum, guar gum and pectin.

In the preparation of the actual reaction product which constitutes the enzyme-dispersible binders employed in this invention, a binder-forming formulation is first prepared. The binder-forming formulation is prepared by blending an organic or aqueous solution, dispersion or emulsion of the reactive group-substituted polymer with a solution or dispersion of the enzyme-degradable polymer. The binder-forming formulation is then applied to a non-woven web and the solvents removed, whereon the reaction between the reactive group-substituted polymer and the enzyme-degradable takes place to form *in situ* the reaction product which constitutes the enzyme-dispersible binder. For example, an enzyme-dispersible binder-forming formulation suitable for use as a binder for the enzyme-dispersible, non-woven webs of the invention is prepared by mixing eight parts by weight of a 15 percent aqueous emulsion of an ethyl acrylate/glycidyl methacrylate copolymer (80/20 mol ratio), prepared as described in example 1 of U.S. Patent 3,507,661, with 92 parts of a 13.5 percent aqueous solution of collagen. The aqueous formulation of reactive group-substituted polymer and enzyme-degradable polymer is then used to prepare the enzyme-dispersible, non-woven fabrics of the invention.

The enzyme-disintegratable binder-forming formulation is applied to the non-woven web to prepare the fabrics of the invention by various processes known to the art, such as, for example, by spraying a solution, emulsion or dispersion of the enzyme-dispersible binder onto the non-woven web; by dipping the non-woven web into a solution, emulsion or dispersion of the enzyme-dispersible binder; or by transfer rolling the solution, emulsion or dispersion to the web. The binder-forming formulation may also be applied to the web during water deposition as in the Fourdrinier process, wherein the binder emulsion or dispersion is present in the process water.

After application of the binder to the web, the web is allowed to dry, whereon reaction of the reactive groups of the reactive group-substituted polymer and the enzyme-degradable polymer takes place with the formation of covalent bonds. This reaction may be accelerated by drying the wet web at elevated temperatures, e.g., 40–70° C., for a short time. Generally, the concentration of enzyme-disintegratable binder in the solution, emulsion or dispersion is adjusted by addition of fluid, e.g., organic solvent, water or aqueous solutions, so that after application to the non-woven web and drying from 0.3 to 100 percent, and preferably one to 15 percent, by weight of the dry fibres of

enzyme-disintegratable binder remains on the web.

The non-woven webs thus formed can have rather high dry tensile strength if desired. Not uncommonly, they have dry tensile strength of the order of 100 to 150 kg./cm². However, dry-strength in excess of 35 kg./cm² is generally not required for most purposes for which the absorbent materials of the invention are to be put. Dry-strength accordingly is relatively unimportant for the webs of the invention. However, when immersed in water, the webs of the invention show wet-strength which can range from 0.5 to 10 kg./cm² or more, depending upon the particular binder which is employed, and the amount of binder which is placed upon the web. Wet-strength is also increased by drying of the wet web and binder at elevated temperatures as set forth above. Preferably wet-strength is 2 to 10 kg./cm². When wet-strength is very low, the non-woven fabrics may disintegrate in water alone after a period of 30 minutes to one hour. However, when wet-strength is higher, it is commonly noted that even after immersion in water for periods of hours or even days, there is very little change in the tensile strength.

For use for various purposes, the webs of the invention are cut, dyed or otherwise shaped to the desired form. They may be folded into multiple layers. In this way, they are conveniently employed for the manufacture of a variety of useful products such as diapers, catamenial bandages, surgical bandages, and disposable washcloths. For disposal, they are readily dispersed into fibers merely by placing in the water in which they are to be disposed an amount of enzyme.

Preferably, cellulose or cellulosic fibers are employed for making the multi-ply structures of the invention.

The absorbent, multi-ply devices of the invention are made from sheets of non-woven materials which are pre-cut in a pre-selected shape or size, according to the purpose for which they are desired. Usefully, the non-woven material is prepared in the form of a roll, and one or more rolls of the material are associated with dies or cutting devices so as to facilitate manufacture in a continuous fashion, in which the webs are drawn from the rolls continuously, brought together in overlying fashion with two or more laminae in contact, and then cut into the pre-selected, appropriate size and shape. Adhesive may be applied to hold the laminae together, or portions of the multi-ply product, e.g. edges or corners, may be pressed together for this purpose, if desired. Thereafter, the multi-ply sheets can be folded, wrapped or packaged in any desired way for convenient handling and sale.

A readily disposable multi-ply pad of the invention consists essentially of an inner body-contacting, self-supporting, water-absorbent lamina composed of a non-woven composite web of fibers having substantially no wet-strength in the absence of binder and in combination therewith a water-insoluble, normally solid, enzyme-degradable binder which consists of a polymer of at least one ethylenically unsaturated monomer covalently bonded with a naturally-occurring enzyme-degradable, water-soluble polymeric material, the polymer having a molecular weight of at least 10,000 and a degree of polymerisation of at least 50, and the binder being present in an effective amount ranging from 0.3 percent to 100 percent by weight of the fibre in the non-woven web, and sufficient to impart to the non-woven web a wet-strength in an aqueous medium in the absence of enzyme of from 0.7 to 50 kg per square centimetre whilst permitting dispersion of the non-woven web in a period ranging from 5 to 30 minutes in an aqueous medium containing an enzyme capable of degrading the water-soluble polymeric material to disintegrate the binder; at least one intermediate lamina of non-woven, moisture-absorbent fibres which contains no binder and has substantially no wet-strength or which contains a binder as defined for the inner lamina; and an outer lamina of a self-supporting, non-woven composite web of material as defined for the inner lamina, having a flexible adherent coating of water-repellent material which is frangible when unsupported; said inner and outer laminae being approximately equal in area and larger than said intermediate lamina or laminae; whereby the pad when in use absorbs body waste liquids without permitting penetration thereof through the outer lamina, and the pad when placed in an aqueous medium containing an enzyme capable of degrading the binder in said inner and outer laminae is rendered completely dispersible and devoid of wet-strength. It will be apparent that the multi-ply structure in use is so placed that the innermost layer contacts the body, and body waste liquids are absorbed in and passed therethrough into the interior lamina or laminae, and are absorbed therein. The water-repellent material prevents passage of moisture all the way through the pad. After use, the entire multi-ply pad is placed in e.g. a domestic flush toilet and an amount of enzyme is added to the water therein. The non-woven plies rapidly disintegrate and can be flushed down the toilet in the usual way, without fear of stoppage. The enzymes do not interfere with the function or efficiency of the domestic sewage disposal system, even with repeated use.

Generally speaking, the self-supporting,

non-woven webs of that application, which are employed here as laminae in the multi-ply product of the present invention, consists of non-woven webs of short fibers of cellulosic or synthetic fibers and the like, e.g., viscose rayon, cotton, wool, silk, cellulose, linen, hemp, wood fibers, regenerated cellulose, nylon and polyester. Preferably, they are natural fibers which are ultimately biodegradable. They are combined with a water-insoluble, normally solid enzyme-disintegratable binder which is sufficient to impart to the non-woven web a web-strength in water in the absence of enzymes of 0.7 to 50 kg./cm².

Exemplary of such binders are reaction products with gelatin disclosed in U.S. patent 3,507,661. The polymers which are reacted with gelatin in these binders have a molecular weight of at least 10,000 and a degree of polymerization of at least 50, and preferably are of a molecular weight such that they have a glass transition temperature (T_g) which is substantially independent of the molecular weight of the polymer. In these binders, the polymer may be a vinyl polymer, and is required to have substituent groups, either pendant or terminal, which are reactive with the water-soluble naturally-occurring polymers. These vinyl polymers can also be termed polymers and copolymers of addition-polymerizable vinyl monomers which have substituent groups reactive with compounds having active hydrogen.

The dispersion of the non-woven webs of the invention for disposal purposes is accomplished by simply wetting the fabric with water containing a suitable enzyme or, possibly more conveniently, by placing the fabric in water and adding thereto a suitable enzyme for disintegration of the binder. The enzyme concentration which is most effective will naturally vary according to the enzyme used and its particular activity upon the binder. The particular enzyme used may require buffered conditions, and this may be accomplished e.g. by including in the dry enzyme preparation an amount of dry buffering agent.

The enzymes which are employed for disposal of the various products of this invention can be any of the well-known classes of enzymes such as hydrolases, oxidases, reductases, transferases and isomerases, which catalyze chemical processes of hydrolysis, oxidation, reduction, group transfer, and isomerization. It may be necessary to buffer the aqueous medium in which they are employed, to obtain the maximum catalytic effect.

The presence of water is in most cases required for enzyme catalysis to be operable. Conditions of pH, ionic strength, and temperature, as well as the presence of additional chemical substances such as

cofactors may also be important in obtaining maximum catalytic effects, depending upon the nature of the individual enzyme and the chemical reaction or process being catalyzed by the enzyme. More complete descriptions of enzymes, their structure and catalytic action are readily available; see, for example, the series of publications "The Enzymes", edited by Paul D. Boyer, Academic Press, New York, or U.S. Patent 3,386,441 which discloses various proteolytic, mucolytic or amylolytic enzymes as applied to catamenial absorbent pads.

Enzymes preferred for the practice of this invention are the hydrolases which catalyze the hydrolysis of a wide range of macromolecular substances to lower molecular weight materials, fragments or units. Hydrolases are relatively innocuous materials, which are used in such common household products as meat tenderizers. Examples of suitable hydrolases are the proteases which catalyze the hydrolysis of proteins to peptides or individual amino acids, e.g., Protease-62 (available from Rohm and Haas Company, hereinafter R and H), Papain, Ficin and Bromelain (available from Miles Laboratories), Trypsin and Chymotrypsin (available from Sigma Chemical Company); polysaccharide hydrolases such as the cellulases which catalyze the hydrolysis of cellulose and many substituted cellulose derivatives to lower molecular weight saccharides, e.g., Cellulase-4000 (available from Miles Laboratories); the pentosanases-hexosanases which catalyze the hydrolysis of gums and mucilages to lower molecular weight polysaccharides and/or sugars, e.g., HP-150 (R and H); and the diastases which catalyze the hydrolysis of starch to carbohydrates of smaller size and less complexity, e.g., Rhozyme-S, -33 and H-39 (R and H).

Using, for example, a somewhat crude enzyme preparation known and available commercially as Protease-62 (a protease catalyzing the hydrolysis of proteins to peptides or individual amino acids), the useful concentration of enzyme in water can vary from about 0.1 to about 0.5 percent, or higher if desired. Preferably the concentrations employed are about 0.05 to about 0.15 percent, whereby disintegration and dispersion of the webs is fast enough from a practical standpoint. Thus, an amount of 1.5 to 3 grams of enzyme is sufficient for use with the average domestic toilet (about 3 liters of water) for each disposal of a diaper, for example. Obviously the use of too much enzyme is wasteful as the corresponding increase in dispersion of the web is not directly proportional to the amount used.

In this way, items made of the composite webs of the invention can be employed for various sanitary purposes and disposed of in ordinary domestic septic tank-type sewage

disposal systems without the use of dangerous and irritating substances, and without causing deleterious effects upon the said systems. Frequently repeated use does not cause build-up of undesirable materials in the said disposal systems. At the same time, the enzymes employed may have a deodorizing or disintegrating effect upon the human wastes which are absorbed, which is also advantageous.

Usefully, an enzyme preparation in dry, powdered form is associated with the item, e.g. a diaper, as by placing it in a fold or closed pocket thereof which does not become wet during use (e.g. in a corner of the diaper). Thus disposal in an aqueous medium conveniently requires no separate addition of enzyme. Other such combination of enzymes with the articles made of the non-woven webs of the invention will readily suggest themselves.

The following examples illustrate the invention and binders employed therein. Parts are by weight unless otherwise specified.

EXAMPLE 1

A non-woven web is produced in a 20 x 20 cm. laboratory model paper sheet former using 4 liters of water and 100 ml. of a dispersion prepared by mixing in a high speed blender 19 parts of 6 mm. RD101 Viscose Rayon Fibers (available from American Viscose Company) and 1900 parts of water containing 0.4 part of "Triton" (Trade Mark) X-100 surfactant (alkylaryl polyether alcohol available from Rohm and Haas Company). After dispelling the water, the sheet formed on the screen is removed on a 20 x 20 cm. piece of blotting paper and dried at 80° C. It has a weight of 24 grams/meter².

An aqueous dispersion of an enzyme-disintegratable binder is prepared by mixing five parts of a 15 percent emulsion of an ethyl acrylate/glycidyl methacrylate copolymer (90/10 mol ratio) (prepared as described in Example 1 of U.S. Patent 3,507,661) with 0.75 part of collagen (e.g. Technical Protein Colloid 5-V, available from Swift and Company) dissolved in 55 parts of warm distilled water adjusted to pH 7.0 to 7.2 with 0.1 N sodium hydroxide solution.

The 20 x 20 cm. non-woven as prepared above is sprayed with 20 ml. of the aqueous dispersion, allowed to dry at room temperature for one hour and then heat cured at 70° C. for two hours. The dried non-woven fabric obtained has a binder content of 52wt. % of the dry fibers of the web and a tensile strength of approximately 263 kg./cm². Wet-strength is about 4.7 kg./cm². Samples of the web when placed in a 0.1 percent solution of Protease-62 (a bacterial

enzyme available from Rohm and Haas Company) buffered to pH 8 and agitated to and fro at room temperature on a mechanical shaker are completely dispersed in 10 to 15 minutes. Samples of the web when agitated in an aqueous solution at pH 8 and room temperature but not containing enzyme required 45 to 75 minutes for dispersal.

- 5 The non-woven web before application of enzyme-disintegratable binder has a tensile strength of about 80 kg./cm² when dry, and when wet with water, the web falls apart completely.

- 10 When samples of the fabric prepared as in Example 1 are agitated in a 0.1 percent solution of Enzyme 56-lot 1 (R and H protease) buffered to a pH of 10, the web disperses completely in 10 minutes at room temperature. Comparable times are also obtained with Enzyme P-53 and Enzyme B-6 (both protease, R and H).

EXAMPLE 2

- 25 A non-woven web is prepared from repulped paper in accordance with the procedure described in Example 1. The non-woven web has a weight of 40 grams/meter² and disperses immediately on contact with water.

- 30 A dispersion of an enzyme-dispersible binder is prepared by mixing an emulsion containing 3.19 g. of an ethylacrylate/glycidyl methacrylate copolymer (90/10 mol ratio, prepared as described in Example 1 of U.S. Patent 3,507,661) in 500 ml. of water with a solution of 3.0 g. of gelatin in 500 ml. of water adjusted to pH 7.5.

- 40 The non-woven web from repulped paper is sprayed to saturation with the above-described enzyme-dispersible binder and air dried. After drying, the treated web is heated in an oven at 40° C. for three hours. Weight gain is less than 1 per cent. The bonded non-woven fabric obtained contains about 1wt. % binder based on the dry fiber and has a dry tensile strength of approximately 133 kg./cm². Wet-strength is from 2.8—3.5 kg./cm². Samples of the enzyme-dispersible binder treated fabric when placed in a 0.1 percent solution of Enzyme 56-lot 1 at pH 10 and room temperature and agitated on a mechanical shaker are completely dispersed in 10 minutes. Comparable dispersion times are also obtained using Enzyme P-53 and Enzyme B-6.

EXAMPLE 3

- 60 Example 1 is repeated using as the enzyme-dispersible binder an aqueous dispersion prepared by mixing 500 ml. of an aqueous emulsion adjusted to pH 7.5 and containing 2.85 g. of an ethyl acrylate/acrolein copolymer (90/10 mol. ratio) with 500 ml. of an aqueous solution containing 3.1 g. of acacia (gum arabic) adjusted to pH 7.5.

The ethyl acrylate/acrolein copolymer used above is prepared by a method analogous to that used for the preparation of ethyl acrylate/glycidyl methacrylate copolymer described in Example 1 of U.S. Patent 3,507,661 using in place of glycidyl methacrylate an equivalent amount of acrolein.

The non-woven fabric prepared in accordance with this example contains 12wt. % binder based on the fiber and disintegrates completely in about 15 minutes when agitated on a mechanical shaker in a 0.1 percent solution of HP-150-mixture 144 (a diastase, R and H).

EXAMPLE 4

A 20 x 20 cm. non-woven viscose fiber web prepared as described in Example 1 is sprayed with 20 ml. of an emulsion prepared by mixing a solution of 0.75 g. of hide glue in 55 ml. of water with 5 ml. of a 15 percent solids latex of a 90/10 ethyl acrylate/glycidyl methacrylate copolymer as described in Example 1. The treated fabric is dried at room temperature for 18 hours and then cured by heating at 75° C. for one hour.

Samples of the non-woven fabric obtained, containing 52wt. % binder based on the fiber, disintegrate completely in 12 to 16 minutes on a mechanical shaker in 0.1 percent solution of Protease-62 that is buffered at pH 9. When agitated in water at pH 9 in the absence of enzyme, 60 to 90 minutes are required to disintegrate the fabric.

EXAMPLE 5

A 20 x 20 cm. non-woven viscose fiber web prepared as described in Example 1 is sprayed with 10 ml. of a one percent solution of gelatin (culture media grade) in water adjusted to pH 7. The gelatin-treated web is air dried and then heated at 60—65° C. for one hour. The dried web is then given a second spraying with 5ml. of a one percent solution of a 65/25/10 methyl methacrylate/ethyl acrylate/glycidyl methacrylate terpolymer (prepared by suspension polymerization according to procedures well-known in the art) in solvent. The terpolymer-treated web is air dried and then cured by heating with a hot iron at 100° C. for 60 seconds.

The bonded non-woven fabric prepared as above has a binder content of 15wt. % based on the fiber and a tensile strength of 187 kg./cm². Wet tensile strength is about 5.2 kg./cm². When agitated in 0.1 percent solution of Protease-62 in tap water, samples of the fabric are dispersed in 3 to 6 minutes. When agitated in water without enzymes, dispersal time is about 70 minutes.

EXAMPLE 6

Bonded non-woven webs are prepared in accordance with the procedure described in Example 5 with the exception that for the

second spraying, 5 ml. of a one percent solution in acetone of a styrene/maleic anhydride copolymer having a molecular weight of about 1000 is used in place of the terpolymer solution. The web is then air dried and cured by heating with a hot iron at 100° C. for 60 seconds.

The bonded non-woven fabric obtained has a binder content of 15wt. % based on the fiber and a dry tensile strength of 237 kg./cm² and a wet tensile strength of 8.4 kg./cm². In 0.1 percent solutions of Protease-62 in tap water, samples of the fabric are dispersed in 6 to 10 minutes. In water without enzymes, dispersal time is from 2 to 6 hours.

EXAMPLE 7

When Example 6 is repeated using a one percent solution in acetone of a methyl vinyl ether/maleic anhydride copolymer (Gantrez AN-119) in place of the one percent acetone solution of styrene/maleic anhydride copolymer, the non-woven fabric obtained has the same binder content and disperses in 11 to 20 minutes when agitated in 0.1 percent solutions of Protease-62. Dispersal time when agitated in water without enzymes is from 2 to 3 hours.

EXAMPLE 8

Preparation of 90/10 vinyl pyrrolidone/glycidyl methacrylate copolymer.

A 3-neck, round bottom flask equipped with a mechanical stirrer, means for maintaining an inert atmosphere, and a thermometer is charged with 395 ml. of distilled water, 22.2 g. (0.2 mol) of N-vinyl pyrrolidone, and 3.10 g. (0.022 mol) of glycidyl methacrylate. The flask is flushed with nitrogen, and the contents are maintained under nitrogen during the course of the reaction. The mixture is stirred, the temperature raised to 50–55° C. and maintained at this temperature, and 0.2 g. of 4, 4'-azobiscyanopentanoic acid is added as polymerization catalyst. As solid material separates from solution during the reaction, acetone (totaling 125 ml.) is added to maintain it in solution. Agitation and heating is maintained for a total of about three hours. At the end of this time the mixture is cooled, and the colorless, syrupy solution is filtered to remove a small amount of insoluble material. The solution obtained contains about 5 percent copolymer. It may be used as such or the polymer may be isolated by spray or drum drying.

EXAMPLE 9

A non-woven web, prepared as in Example 1, is sprayed with 20 ml. of an aqueous solution adjusted to pH 7 of 1 g. of hide glue and 1 g. of a 90/10 N-vinyl pyrrolidone/glycidyl methacrylate copolymer (prepared

as described in Example 8) in 200 ml. of water. The treated web is air dried and cured by heating with a hot iron at 100° C. for 30 seconds, giving a binder content of 21wt. % based on the fiber. When agitated in 0.1 percent solutions of Protease-62 in water, the dispersal time is 12 to 14 minutes. When agitated in water without enzyme, dispersal time is 50 to 65 minutes.

EXAMPLE 10

Preparation of 90/10 vinyl pyrrolidone/acrolein copolymer.

3-neck, round bottom flask equipped with a mechanical stirrer, means for maintaining an inert atmosphere in the flask and a thermometer is charged with 368 ml. of distilled water, 22.2 g. (0.2 mol) N-vinyl pyrrolidone and 1.3 g. (0.02 mol) of acrolein. The flask is flushed with nitrogen, and the contents of the flask are maintained under nitrogen during the course of the reaction. The mixture is stirred, the temperature is raised to 50–55° C. and maintained at this temperature, and 0.2 g. of 4, 4'-azobiscyanopentanoic acid is added. After two hours reaction an additional 0.2 g. of 4, 4'-azobiscyanopentanoic acid is added, and the reaction is allowed to continue for an additional three hours. At the end of this time, the mixture is filtered to remove a small amount of insoluble material. The filtrate obtained contains about 6 percent by weight of copolymer. The solution may be used as such or isolated by spray or drum drying.

EXAMPLE 11

Example 7 is repeated using 1 g. or 90/10 N-vinyl pyrrolidone/acrolein copolymer (prepared as described in Example 10) in place of 1 g. of 90/10 N-vinyl pyrrolidone/glycidyl methacrylate copolymer.

The non-woven fabric obtained has the same binder content as in Example 9 and a dispersal time in aqueous one percent Protease-62 solution of 4 to 5 minutes. In the absence of Protease-62, the dispersal time in water is greater than 6 hours.

EXAMPLE 12

A non-woven web prepared as in Example 1 is sprayed with 20 ml. of an aqueous solution prepared by dissolving 1 gram of edible grade corn starch in hot water, cooling to room temperature, adding 1 g. of 90/10 N-vinyl pyrrolidone/acrolein copolymer (prepared as described in Example 10) and diluting the mixed solution to 200 ml.

The non-woven fabric obtained has a binder content of 21wt. % based on the fiber and a dispersal time when agitated in aqueous 0.1 percent Protease-62 of 30 to 40 minutes. (Protease-62, a bacterial enzyme

preparation, contains only a low diastase or starch-liquefying activity.) When samples of the fabric are agitated in 0.1 percent of Rhozyme-S, a diastase enzyme, the dispersal time is 12 to 15 minutes. In the absence of enzymes, dispersal time of the fabric is 60 to 65 minutes.

A diaper having the property of being dispersible in enzyme solution may be constructed in the following manner.

A binder solution is first prepared from 21 parts of hide glue, 7.5 parts of a polymer latex containing 30 percent solids by weight of a copolymer of 90 parts ethylacrylate and 10 parts of glycidyl methacrylate prepared as described in U.S. patent 3,507,661, and 400 parts of distilled water. Several 46 cm. x 36 cm. paperlike, non-woven sheets of basis weight 24 g./cm² of viscose rayon fiber are saturated with the solution and allowed to air dry. These sheets are then cured at 100° C. for 3 to 5 minutes in an oven.

After curing, the sheets are desirably treated with a softening agent, such as glycerol. For this purpose, they are saturated with a mixture of 120 parts of glycerol and 100 parts of water by weight, and dried on a paper dryer at 65° C. If desired a small amount of starch, e.g. 10 grams, can be added to the softener. Half of the sheets are then brush coated with molten microcrystalline wax (available under the trademark Shellmax 500) at a temperature of 63°—65° C. to form a thin, flexible, water-repellent coating. The temperature must be high enough to make the wax coat-able, yet low enough to prevent significant penetration of the web.

A sheet of wax-coated material is laid wax side up on a flat surface, and about 25 to 35 g. of wood pulp fluff is evenly spread upon all but about a 6 cm. border around the edge. One of the unwaxed sheets is then placed on the top of this, and the edges are heat-sealed with a warm iron.

The diaper or absorbent pad thus made is a multi-ply product. It is further described as follows: In flat, unfolded position, in the condition in which all plies are approximated, the diaper has three plies or laminae. The non-woven material of these laminae are soft and of low resilience and have an uncalendered surface so as to cause the respective plies to cling together when pressed together along the edges sufficiently to withstand normal handling and folding without separating. The innermost, body-contacting ply is composed of a non-woven web of relatively short cellulose fibers having substantially no wet-strength in the absence of binder, and which has an enzyme-degradable, normally solid, water-insoluble binder therein which consists of a polymer of at least one ethylenically unsaturated monomer covalently bonded with a naturally-

occurring, enzyme-degradable, water-soluble polymeric material having a molecular weight of at least 10,000 and a degree of polymerization of at least 50, which is present in an effective amount ranging from 0.3 percent to 100 percent by weight of said fiber in the non-woven web. Enough binder is used to give the non-woven web wet-strength in water, in the absence of enzyme, of 0.7 to 50 kg/cm². The web is dispersible in an aqueous medium containing an enzyme in 5 to 30 minutes.

The intermediate ply consists of non-woven web which is substantially without wet-strength, or which has binder as described for the innermost ply. This ply is preferably of lower density, or higher loftiness, and is highly absorbent of body fluids when in use, i.e., it has a wicking action and the ability to absorb and hold 100 to 300 ml. of fluid. The size of this intermediate ply is preferably made smaller in all dimensions than the inner and outer plies, so as to be overlapped by them on all sides. A useful material for the purpose is creped tissue paper or a similar bat of cellulosic fibers.

The outermost ply is made of the same material as the innermost, body-contacting ply but has on its surface a flexible coating of 25 to 125 microns in thickness of wax, said outermost ply having a tensile strength from 0.5 to 25 kg/cm². Typical waxes useful for the purpose include microcrystalline wax, ozokerite, paraffin wax, beeswax, tallow and waxy polyvinyl esters of fatty acids which have been modified by the incorporation of up to 25 percent of a flexible modifier to provide suitable flexibility and tensile strength to the wax. Typical flexibility modifiers include petrolatum and low molecular weight polymers and copolymers such as polyvinylacetate, polyethylene and ethylene-methacrylate copolymer. Thin films and coatings of such waxy materials have little strength or film-forming properties when unsupported. The function of this coating is to prevent passage of body fluids through the outermost layer, while withstanding a reasonable amount of folding and bending. The coating is made thin so that it will not flake off. The coating does not penetrate the thickness of the ply to any material extent, so that when the uncoated surface of the outer ply is contacted with aqueous enzyme solution, the web disintegrates and disperses from that side, leaving the water-repellent coating unsupported. In this condition it readily fractures and disperses with slight agitation. Such frangible coatings are preferred.

It will of course be apparent that the water-repellent coating can alternatively be placed on the outer side of the outermost ply with similar results.

The assembly of plies is preferably pressed together at the edges to cause the laminae to adhere sufficiently to withstand normal handling while in dry condition. Typical thickness for each ply is as follows: inner ply, 0.1 mm.; absorbent ply, 5 mm.; outer ply, 0.15 mm., including the coating of waxy material. Obviously these can be made thicker or thinner as required for any specific use.

A diaper of this construction can be folded appropriately and fastened about an infant using safety pins or other fastening means. The diaper when in use absorbs body waste liquids without permitting penetration thereof through said outer layer. After being soiled, the diaper is placed into an ordinary domestic flush toilet bowl along with 2 to 3 grams of a proteolytic enzyme (e.g. that available under the trademark Protease 62). After 5 to 10 minutes the diaper is essentially without any wet strength and completely dispersible, and may be completely flushed away without danger of clogging the sewer system.

WHAT WE CLAIM IS:—

1. A self-supporting, non-woven composite web which is dispersible in an aqueous medium containing an enzyme, consisting essentially of a non-woven web of fibres and in combination therewith a water-insoluble, normally solid, enzyme-disintegratable binder which consists of a polymer of at least one ethylenically unsaturated monomer covalently bonded with a naturally-occurring, enzyme-degradable, water-soluble polymeric material, the binder being present in an effective amount ranging from 0.3 percent to 100 percent by weight of the fibres in the non-woven web, sufficient to impart to the non-woven web a wet-strength in an aqueous medium in the absence of an enzyme of at least 0.5 kg./cm² and to increase the resistance to dispersion of the web in plain water whilst permitting dispersion of the non-woven web in a period ranging from 5 to 30 minutes in an aqueous medium containing an enzyme capable of disintegrating said binder.

2. A composite web according to claim 1 wherein the enzyme-degradable water-soluble polymeric material is selected from proteins.

3. A composite web according to claim 1 in which the enzyme-degradable, water-soluble polymeric material is a film-forming polysaccharide.

4. A composite web according to claim 1 in which the polymer has a molecular weight of at least 10,000 and a degree of polymerisation of at least 50 and is covalently bonded directly to gelatin.

5. A composite web according to claim 1 in which the polymer is a copolymer con-

taining recurring vinyl or vinylidene monomer units, from 5 to 30 mole percent of said monomer units having at least one group reactive with an active hydrogen atom.

6. A composite web according to claim 5 in which the naturally-occurring polymer is gelatin.

7. A composite web according to any of claims 1 to 6 in which the fibres are viscose rayon fibres.

8. A composite web according to any of claims 1 to 6 in which the fibres are wood pulp fibres.

9. A composite web according to claim 1 in which the binder is an ethyl acrylate/glycidyl methacrylate copolymer in 90/10 mole ratio covalently bonded with gelatin.

10. A composite web according to claim 14 in which the binder is an ethyl acrylate/acrolein copolymer in 90/10 mole ratio covalently bonded with gum arabic.

11. A composite web according to claim 1 in which the binder consists of a terpolymer of methyl methacrylate/ethyl acrylate/glycidyl methacrylate in 65/25/10 ratio covalently bonded with gelatin.

12. A composite web according to claim 1 in which the binder is a methyl vinyl ether/maleic anhydride copolymer covalently bonded with gelatin.

13. A composite web according to claim 1 in which the binder is a styrene/maleic anhydride copolymer covalently bonded with gelatin.

14. A composite web according to claim 1 in which the binder is a N-vinyl pyrrolidone/acrolein copolymer in 90/10 ratio covalently bonded with corn starch.

15. A composite web according to claim 1 containing binder in an effective amount of from 1 to 15 percent by weight of the dry fiber.

16. A composite web according to claim 1 having a wet-strength in an aqueous medium in the absence of enzyme ranging from 2 to 10 kg./cm².

17. A process for disposing of a composite web according to any of claims 1 to 16 which comprises gently agitating said composite web in an aqueous medium in the presence of an enzyme capable of disintegrating said binder over a time period ranging from 5 to 30 minutes.

18. A process according to claim 17 in which the binder contains gelatin and the enzyme is a protease.

19. A process according to claim 17 in which the binder contains a polysaccharide and the enzyme is a polysaccharide hydrolase.

20. An article of manufacture, consisting of a composite web according to any of claims 1 to 16 including an amount of a dry enzyme preparation capable of degrading the binder, the said enzyme being associated

with the web at a location such that the enzyme preparation does not become wetted by aqueous fluid during normal use of said article.

5 21. An article according to claim 20 comprising a diaper having a closed pocket containing said enzyme preparation in a corner of said diaper.

10 22. A disposable multi-ply pad for contacting the body and absorbing body wastes, which comprises an inner body-contacting, self-supporting, water-absorbent lamina composed of a non-woven composite web of fibers having substantially no wet-strength
15 in the absence of binder and in combination therewith a water-insoluble, normally solid, enzyme-degradable binder which consists of a polymer of at least one ethylenically unsaturated monomer covalently bonded with
20 a naturally-occurring, enzyme-degradable, water-soluble polymeric material, the polymer having a molecular weight of at least 10,000 and a degree of polymerization of at least 50, and the binder being present
25 in an effective amount ranging from 0.3 percent to 100 percent by weight of the fiber in the non-woven web, and sufficient to impart to the non-woven web a wet-strength in an aqueous medium in the absence of
30 enzyme of from 0.7 to 50 kg per square centimetre whilst permitting dispersion of the non-woven web in a period ranging from 5 to 30 minutes in an aqueous medium containing an enzyme capable of degrading the
35 water-soluble polymeric material to disintegrate the binder; at least one intermediate

lamina of non-woven, moisture-absorbent fibres which contains no binder and has substantially no wet-strength or which contains a binder as defined for the inner lamina; and an outer lamina of a self-supporting, non-woven composite web of material as defined for the inner lamina, having a flexible adherent coating of water-repellent material which is frangible when unsupported; said inner and outer laminae being approximately equal in area and larger than said intermediate lamina or laminae; whereby the pad when in use absorbs body waste liquids without permitting penetration thereof through the outer lamina, and the pad when placed in an aqueous medium containing an enzyme capable of degrading the binder in said inner and outer laminae is rendered completely dispersible and devoid of wet-strength.

23. A dispersible non-woven composite web substantially as hereinbefore described in any one of Examples 1 to 7, 9, 11 and 12.

24. A process for disposing of a web according to claim 23 substantially as hereinbefore described.

25. A disposable absorbent multi-ply according to claim 22 substantially as
65 hereinbefore described.

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